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Low cost auxiliary system for broadband NMR on strongly magnetic systems

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A low cost auxiliary system consisting of He cryostat, superconducting magnet, and sample holder assembly with field probe has been constructed. The system meets the requirements of NMR on strongly paramagnetic or ordered magnetic materials, which are accurate temperature settings over a wide range, high NMR frequencies, high and accurate magnetic fields of moderate homogeneity, and exact crystal orientations in the fields. The following values are achieved: The temperature setting in the range 1.7–400 K varies less than 0.5% for 10 min, which is the typical recording time of a spectrum. The distance from the NMR oscillator to the sample is only 55 cm (wavelength of $\sim$550 MHz radiation), giving a tolerable He evaporation rate of 0.35 l/h. The maximum field at 4.2 K is 43.2 kG, which can be measured with an accuracy better than $\pm$100 ppm. The homogeneity at maximum field over a central sphere 8 mm in diameter is 5 G. The uncertainty on the crystal orientation in the field is $\pm$1/2 degree.

INTRODUCTION

Many papers describing systems for producing[1-4] and measuring,[5,6] magnetic fields at samples in superconducting magnets, as well as for setting[7-10] and maintaining[11] sample temperatures are found in the literature. The NMR auxiliary system to be described here, however, is designed especially for measurements on strongly paramagnetic or ordered magnetic materials. The subject of the studies is either the hyperfine coupling of the paramagnetic ion to its own nucleus or the transferred hyperfine coupling to the ligand nuclei.[12,13] The matching VHF NMR oscillators will not be discussed, but rather the construction for achieving a large field and temperature range and accurate setting of sample temperature, field strength, and field orientation.

The NMR parameters of interest in these studies are mostly small line shifts ΔH, depending on the temperature T, the field H, and the angle θ between the field and the main crystal axis. The dependence is frequently of the form

$$\Delta H = C \cos^2\theta T^{-1} H, \quad (1)$$

with C being of the order of one kelvin. Also the NMR line width δH is of interest. δH is often only slightly field dependent, but strongly temperature dependent, having values from 10 G up to several kilogauss. These properties determine the requirements: ΔH calls for accurate setting of temperature, absolute field, and orientation of the crystal in the field. δH necessitates high but only moderate homogeneous field. High fields also lead to high NMR frequencies.

The system (which is shown in Fig. 1) consists of the cryostat, the superconducting magnet, and the sample holder assembly including the NMR field probe.

I. CRYOSTAT

The permanently evacuated outer stainless-steel Dewar for liquid N_2 is 987 mm long overall and 248 mm in diameter. The N_2 refilling is automatic, and the consumption is 40 l for cooling down and 15 l/day in continuous use. The inner glass Dewar for liquid He is 690 mm long and has 160 mm i.d. The vacuum space can be pumped allowing fast cool down to liquid N_2 temperatures (5 h) and efficient isolation at lower temperatures. The He level is continuously monitored by a floating stick. The cooling power of the evaporating He gas is well utilized by five thin, tight-fitting chromium plated combined stream breakers and radiation shields distributed along the sample compartment tube. The first cooling down and filling takes 8 l of He, after which the zero-field evaporation rate is 0.35 l/h, rising to 0.40 l/h for maximum field. Overnight warm up is approximately to 35 K and renewed cooling and filling takes 6.5 l. Experiments below 4.2 K are performed with the pressure of the He bath pumped down to 9 mm Hg, and thus keeping the temperature of the bath and the magnet at 1.7 K. The pumping is performed by an Alcatel He pump with a capacity of 30 m³/h. Cooling to 1.7 K takes 2.5 l of He, after which the evaporation rate is the same as at 4.2 K. At the low temperature the maximum field of the magnet rises significantly over the 43 kG at 4.2 K. The rather short distance from the top flange to the center of the magnet of 530 mm is a compromise between the conflicting requirements of high-frequency NMR and He economy.

II. SUPERCONDUCTING MAGNET

The split coil superconducting solenoid is wound on a one piece G-etronax glass fiber bobbin reinforced with

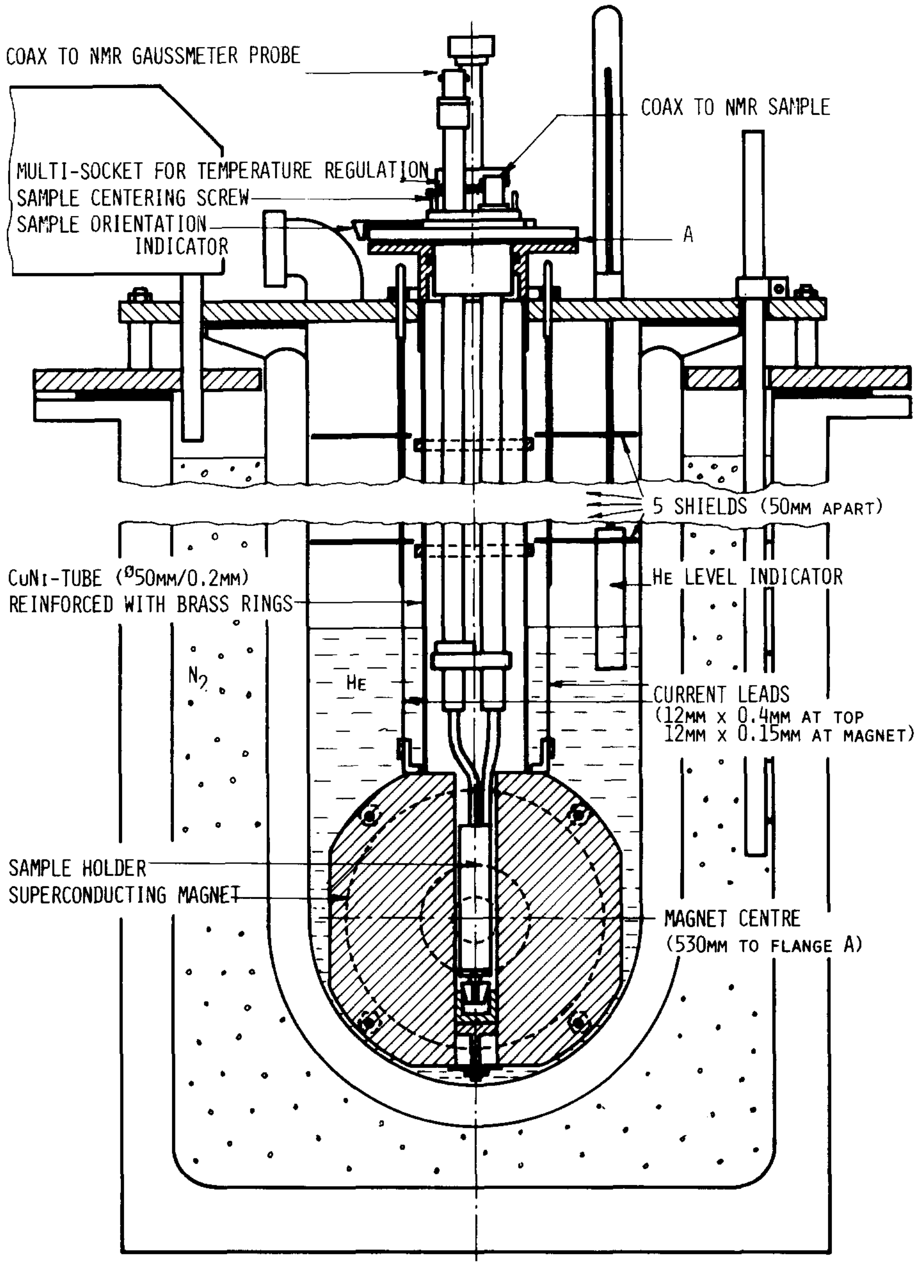

FIG. 1. The entire NMR auxiliary system consisting of cryostat, magnet, and sample holder assembly.

four corner bolts before removal from the winding device. The solenoid has the dimensions shown in Fig. 2 and is made from 0.33-mm-diam Niomax-FM superconducting wire consisting of 61 copper clad filaments of the composition 44 wt.% Nb, 56 wt.% Ti, using ~1.5 km of wire, corresponding to 7348 turns distributed with 3674 in each coil. Two criteria for the dimensioning have been applied: (1) The homogeneity δH_m in a central sphere of 8 mm in diameter should be somewhat better than the smallest line width in our type of experiments, $\delta H \approx 10$ G. (2) The ratio R of the central field to the highest field in the wire region should be maximum. For the final magnet we find $\delta H_m/H = 110$ ppm, $R = 0.80$, and the maximum central field at 4.2 K before quench $H_{max}{}^C = 43.2$ kG. This corresponds to maximum $\delta H_m = 4.8$ G and maximum field in the windings 54 kG. The current consumption is 1.09 A/kG central field.

The sample compartment, which also serves as support for the magnet, has a main upper part consisting of 0.2-mm thin-walled Cu–Ni alloy tube of low heat conduction. In order to resist the outer pressure when evacuated, it is reinforced with brass rings, which also carry the shields. The lower part of the compartment is made from brass in order to be nonmagnetic. The copper leads for the magnet current are flat and tapered, being 12 × 0.4 mm at the top flange and 12 × 0.15 mm at the magnet. The available cylindrical space in the magnet assembly is 21 mm in diameter. The copper coils for modulation (3 mm broad and 18 mm in diameter) are fitted in a central bore through the magnet bobbin, touching the sample compartment. 200 G peak-to-peak modulation can be attained without detectable extra He evaporation.

III. SAMPLE HOLDER ASSEMBLY

The sample holder assembly consists of the top flange, the coaxial lines, and the sample holder. The top flange

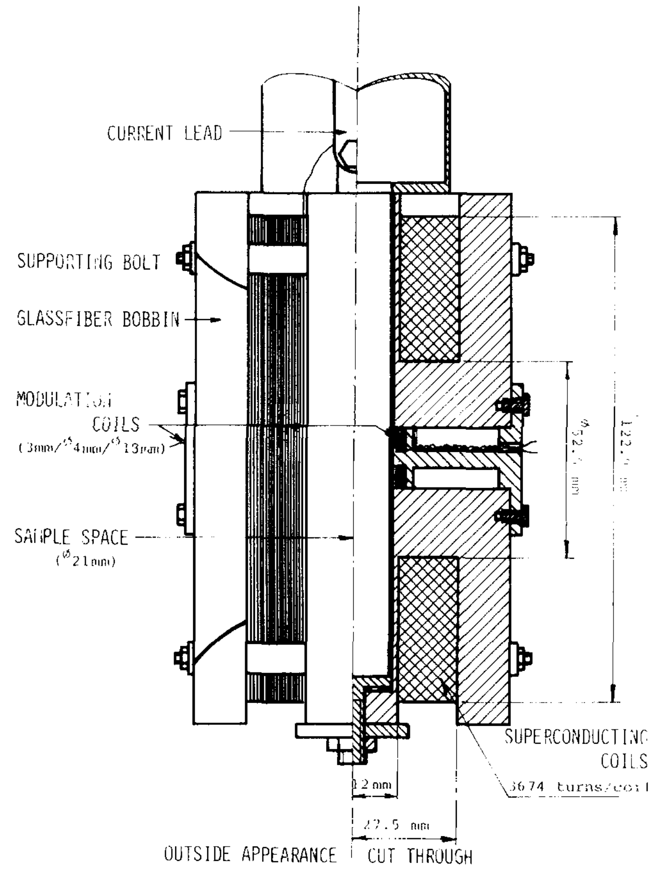

FIG. 2. The superconducting magnet including the field modulation coils. To the left and the right the outer appearance and a cross section, respectively, are shown.

carries a pointer for setting the sample orientation, an 18-pin socket for the temperature regulation, and two BNC-sockets for the sample NMR signal and for the gaussmeter NMR signal.

The sample holder is shown in Fig. 3. The base, which is made from copper, has a slightly conical central bore for a cylinder 3 mm in diameter and 8 mm long on which the sample is glued with low-temperature Araldite. Spherical samples are always required in these types of experiments in order to have simple demagnetization conditions. The diameter is typically between 2 and 6 mm. The sample is x-ray preorientated on the cylinder, but up to 2° final x-ray adjustment is possible directly in the sample holder using microscrews. A self-supporting coil of few turns lacquered copper wire is fitted tightly around the sample and connected to the coaxial line leading to the NMR oscillator. The NMR gaussmeter probe consists of an Araldite moulded cylinder of 30-μm Al powder, 3 mm long and 3 mm in diameter. It is completely shielded in a cylindrical metal housing, which terminates the gaussmeter coaxial line. This arrangement can be pushed in place directly on top of the sample. The distance between the sample and gaussmeter probe centers varies between 3 and 5 mm depending on sample size. The top flange carries screws for placing the sample and gaussmeter-probe symmetrically around the magnet center.

Temperatures above 30 K are determined from a four-point resistance measurement on a copper wire 2 m long and 0.02 mm in diameter bifilar wound in a groove in the sample holder base. Temperatures below 30 K are monitored similarly using an Allen–Bradley carbon resistor and a Lake Shore Cryotronics germanium resistor. The time stable germanium resistor is used for each temperature setting to calibrate the carbon resistor in zero field. The temperature is then monitored and maintained in the applied field using the field independent carbon resistor. The cylindrical germanium and carbon resistors are placed in horizontal bores in the base situated less than 5 mm from the sample.

The copper sensor and the low-temperature sensors are, respectively, constant current and constant voltage fed due to the opposite temperature slopes of their resistance. The temperature regulator[14] compares the response from the sensors with a voltage on a ten turn precision potentiometer setting the temperature, and maintains the temperature setting by feeding current through a copper heating wire, bifilar wound on a brass tube mounted around the sample holder. The varying resist-

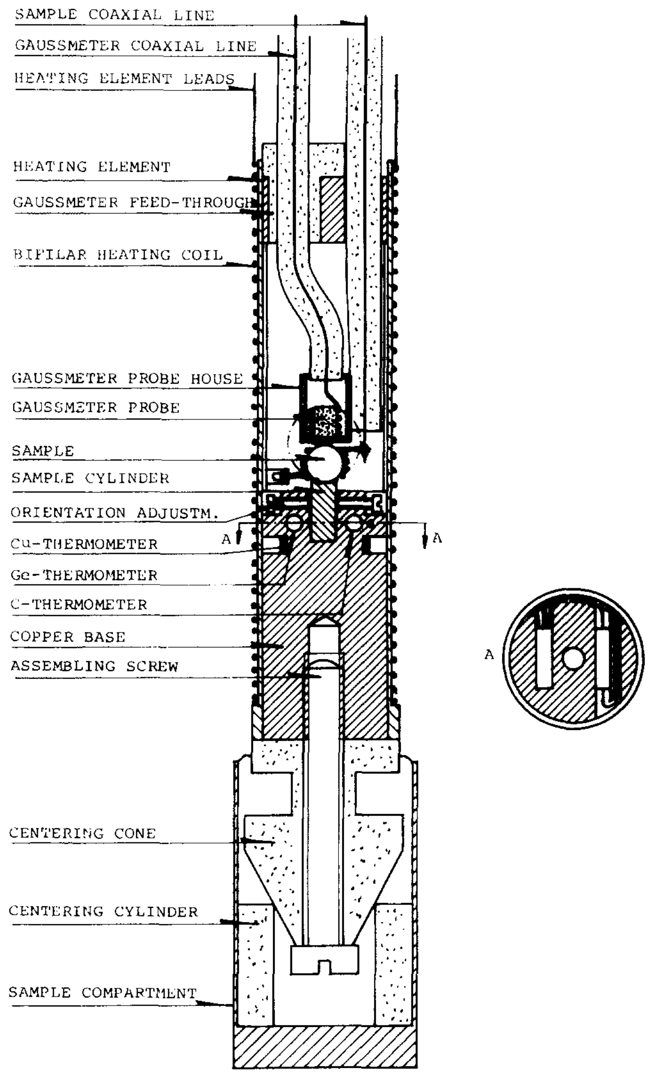

FIG. 3. The sample holder including NMR field probe and temperature regulation. (The dot-and-dash circle indicates the 8-mm-diam central sphere).

ance of the copper wire is advantageous, leading to high heating power at high temperatures, where it is most needed. At low temperatures an exchange He gas pressure up to 5 mm Hg in the sample compartment is demanded. At temperatures above ~50 K, vacuum better than 1 μm Hg is required. The temperature setting is kept to within 0.5% in the whole temperature region during the time of an NMR spectral scan, which is typically 10 min. The temperature is reproducible within the same limits from day to day or when a different vacuum/heating combination is used, as judged from the appearance of the NMR spectrum in special temperature test runs.

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[1] M. S. Lubell, Cryogenics **12**, 340 (1972).
[2] S. I. Goridov, L. S. Lazareva, and V. N. Morgun, Cryogenics **13**, 55 (1973).
[3] K. Kaiho, T. Namba, T. Ohara, and K. Koyama, Cryogenics **16**, 587 (1976).
[4] G. Reményi, I. Kirschner, and T. Porjesz, Cryogenics **17**, 565 (1977).
[5] E. M. Dickson, Rev. Sci. Instrum. **43**, 1381 (1972).
[6] W. R. Wampler, S. Matula, B. Lengeler, and G. Durcansky, Rev. Sci. Instrum. **46**, 58 (1975).
[7] H. H. Sample, L. J. Neuringer, and L. G. Rubin, Rev. Sci. Instrum. **45**, 64 (1974).
[8] D. L. Swartz and J. M. Swartz, Cryogenics **14**, 67 (1974).
[9] P. H. Kes, C. A. M. van der Klein, and D. de Klerk, Cryogenics **14**, 168 (1974).
[10] H. H. Sample and L. G. Rubin, Cryogenics **17**, 597 (1977).
[11] J. Sthanapati and S. N. Bhattacharyya, Cryogenics **16**, 735 (1976).
[12] P. E. Hansen and R. Nevald, Phys. Rev. B **16**, 146 (1977).
[13] P. E. Hansen and R. Nevald, Phys. Rev. B **17**, 2866 (1978).
[14] K. G. Nielsen (design unpublished).